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Polyanilines have been known for over one hundred years. Recent studies of this chemically flexible polymer have demonstrated unusual chemical, electrical, and optical phenomena, both in insulating forms and conducting forms. Polyaniline has three stable insulating forms, leucoemeraldine base (LEB), emeraldine base (EB), and pernigraniline base (PNB). These three forms exhibit differing phenomena ranging from intramonomer luminescing excitons and ring rotation polarons in LEB, to nonluminescing charge transfer excitons and also ring rotational polarons in EB, to a degenerate ground state with bond order parameter solitons and ring order parameter polarons in PNB. The LEB form can be p-doped (oxidatively doped), the EB form can be protonic acid doped and the PNB form can be n-doped (reductively doped) to form conducting systems. Charge conduction studies of oriented films and fibers demonstrate that three-dimensional order between chains is critical for high conductivities. The ability to derivatize polyaniline at ring and nitrogen positions allows one to test concepts for the control of conductivity as well as improved processing.

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"ELECTRONIC PHENOMENA IN POLYANILINES"

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Electronic Phenomena in Polyanilines

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ABSTRACT

Polyanilines have been known for over one hundred years. Recent studies of
this chemically flexible polymer have demonstrated unusual chemical,
electrical, and optical phenomena, both in insulating forms and conducting
forms. Polyaniline has three stable insulating forms, leucoemeraldine base
(LEB), emeraldine base (EB), and pernigraniline base (PNB). These three forms
exhibit differing phenomena ranging from intramonomer luminescing excitons
and ring rotation polarons in LEB, to nonluminescing charge transfer excitons
and also ring rotations polarons in EB, to a degenerate ground state with bond
order parameter solitons and ring order parameter polarons in PNB. The LEB
form can be p-doped (oxidatively doped), the EB form can be protonic acid doped
and the PNB form can be n-doped (reductively doped) to form conducting
systems. Charge conduction studies of oriented films and fibers demonstrate
that three-dimensional order between chains is critical for high conductivities.
The ability to derivatize polyaniline at ring and nitrogen positions allows one to
test concepts for the control of conductivity as well as improved processing.

FREQUENCY RESPONSE

DC	ELECTROSTATIC ELIMINATION ($10^{-8} \Rightarrow 10^{-2}$ S/cm)
	AIRCRAFT STRUCTURES
	ANODIZE SURFACES
	CONDUCTING WIRES (>10^4 S/cm)
	TIME-TEMPERATURE-ENVIRONMENT INDICATORS
	SWITCHES
10^0	*BIOLOGICAL SUBSTRATES*
	MEMBRANES (GAS SEPARATION) } ELECTROCHEMICAL
10^2	ELECTROCHROMICS, BATTERIES }
	pH MODULATORS
	SMART WINDOWS, SENSORS } RESPONSE
10^4	*ACTIVE ELECTRONICS (DIODES, TRANSISTORS, ...)*
	ELECTROMAGNETIC INTERFERENCE (EMI) SHIELDING
10^6	
10^8	
	REMOTE HEATING
10^{10}	MICROWAVE ABSORPTION (TAN $\delta \geq 10^{-1}$)
	WELDING OF PLASTIC JOINTS
10^{12}	
	NONLINEAR OPTICS ($\sim 10^{-12}$ SEC)
10^{14}	*ERASABLE OPTICAL INFORMATION STORAGE ($\sim 10^7$ SEC)*
10^{16}	
Hz	

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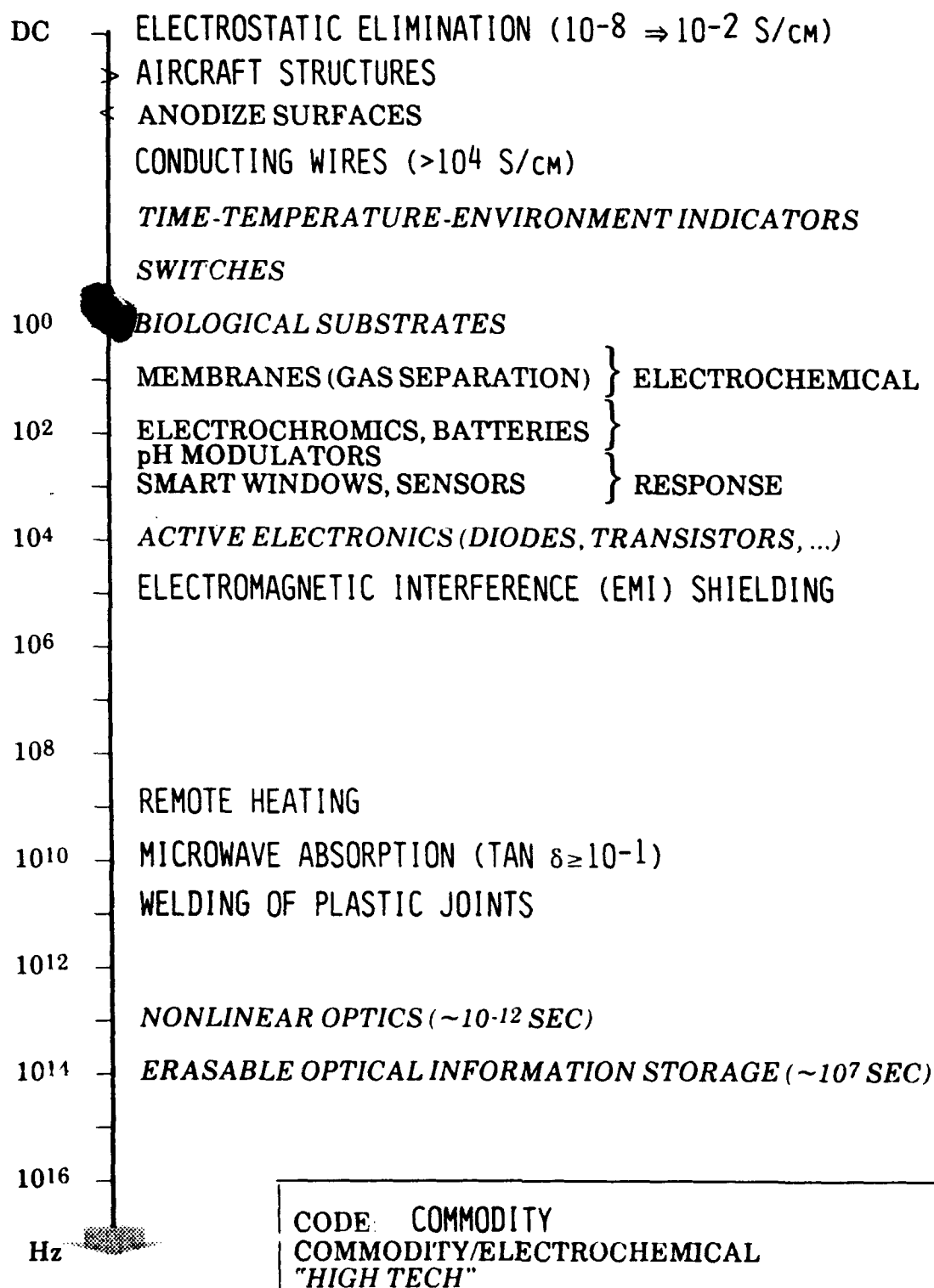COMMODITY/ELECTROCHEMICAL
"HIGH TECH"

Fig. 1 Potential applications of electronic polymers.

INTRODUCTION

The polyanilines are among the oldest known synthetic organic polymers, having been first reported in 1862 [1]. Since the mid-1980's there has been a mushrooming interest in this family of polymers [2-8]. Synthesis of polyanilines and their derivatives have been extensively described [7]. The facile chemistry of this system and its ability to be processed into oriented films [9,10] and fibers [11-13] have opened the opportunity to design in properties for function. This has lead to interest in the potential use of polyanilines and related conducting polymers in a variety of commodity, commodity/electrochemical, and high tech type applications [14, 15]. Figure 1 summarizes the range of technologies proposed. It is noted that a wide range of resistivities from insulating through highly conducting are of potential utility.

We review here the essential differences in the physics of the three different polyaniline insulating forms as well as present a summary of the critical aspects controlling conductivity in the emeraldine salt system. The effects of derivatization are briefly indicated. The parent polyaniline can be prepared in a range of oxidation states ranging from the fully reduced form, leuceoemeraldine base (LEB), $\{NH\text{-}C_6H_4\text{-}NH\text{-}C_6H_4\}_x$, (Fig. 2a.), to the fifty percent oxidized emeraldine base (EB), $\{NH\text{-}C_6H_4\text{-}NH\text{-}C_6H_4\text{-}N = C_6H_4 = N\text{-}C_6H_4\}$ (Fig. 2b), to the fully oxidized pernigranilne base (PNB), $\{N = C_6H_4 = N\text{-}C_6H_4\}_x$ (Fig. 2c) [7,16]. The three base forms are insulators. Protonation of EB or oxidation of LEB leads to formation of the conducting emeraldine salt (ES) shown in Fig. 2d as the hydrochloride salt.
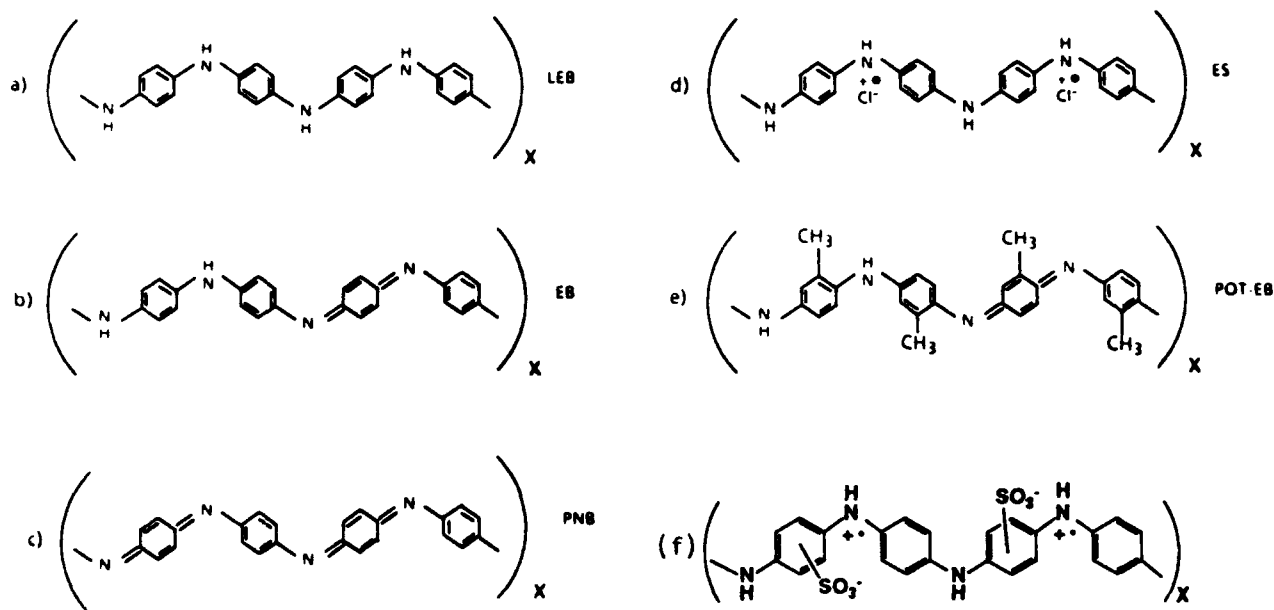

Fig.2. (a) leucoemeraldine base; (b) emeraldine base; (c) pernigraniline base; (d) emeraldine hydrochloride salt polymer; (e) poly(orthotoluidine) (emeraldine base form); (f) sulfonated polyaniline (self-doped form).

DERIVATIZATION

The polyanilines are easily derivatized at the ring [17-19] and nitrogen [20] positions. For example, replacement of one H of each ring with a CH_3 group to form poly (o-toluidine), Fig. 2e, enables testing of the roles of interchain separation and crystalline order in determining electronic properties [17,21,22], while replacement of a H on one-half the rings with a sulfonic acid group, $-SO_3H$, Fig. 2f, leads to a self-doped polymer the conductivity of which is independent of pH for pH $\lesssim 7.5$ [18,19] (Fig. 3) and exhibits greater thermal and environmental stability [23]. The change in doping level with temperature for emeraldine hychloride and ring-sulfonated polyaniline is estimated by assuming that the entire weight loss measured by thermogravimetry is due to loss of HCl and SO_3H, respectively, Fig. 4. In actuality, loss of polymer fragments may occur as well.
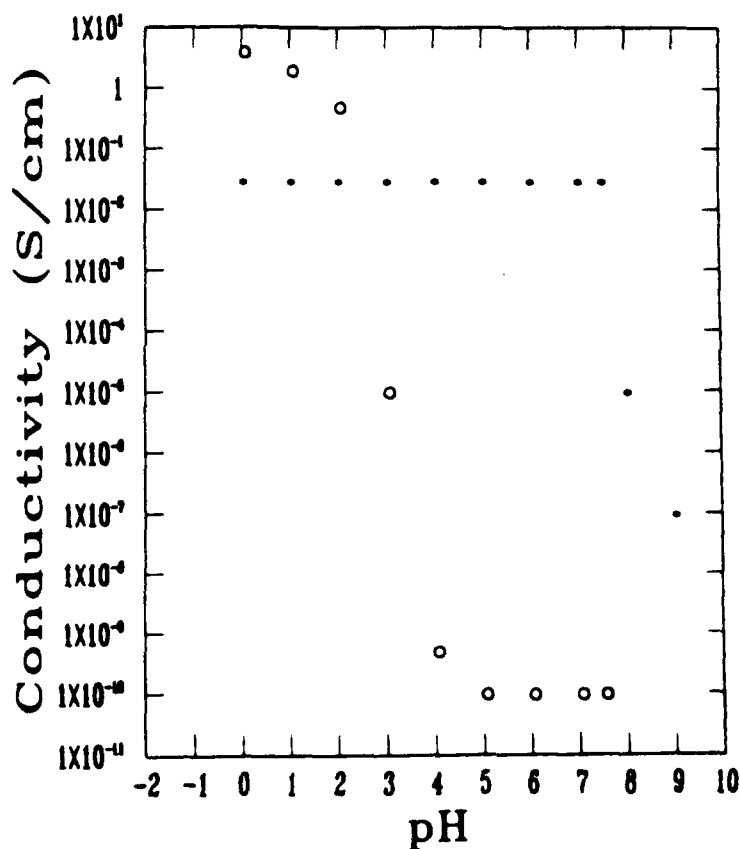

Fig. 3. pH dependence of conductivity of ring-sulfonated polyanilines (*) and the emeraldine hydrochloride form of polyaniline (o) (from Ref. 19).
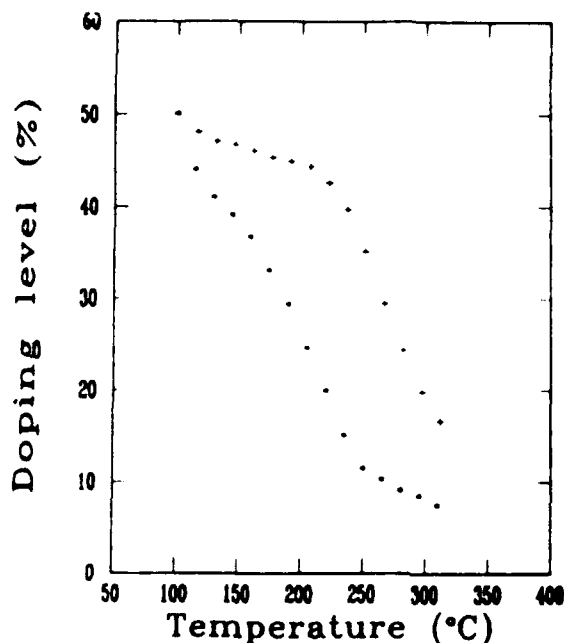
Fig. 4. Doping levels determined by
thermogravimetry of emeraldine
hydrochloride (*) and sulfonated
polyaniline (+) as a function of
temperature assuming that the entire
weight loss for each polymer is due
only to loss of HCl and SO_3H
respectively (from Ref. 23).

SPECTROSCOPY AND PHOTOEXCITATION SPECTROSCOPY

The optical absorption spectrum of LEB [24] is shown in Fig. 5 together with
the results of a Hückel calculation for the electronic band structure of LEB
carried out assuming that the repeat unit is a single (C_6H_4NH) unit [25,26]. This
simple calculation reproduces most of the band structure features obtained in
more extensive calculations [27,28,29]. The seven energy bands are derived from
the six p_z energy levels of benzene together with the p_z energy level
of nitrogen. The lower four energy bands are completely filled while the upper
three are empty. It is noted that the valence band is relatively broad (its breadth
depending upon the ring torsion angle) while the conduction band is
dispersionless. Hence, charge conjugation symmetry is absent in
leucoemeraldine base. The exact width and separation of each of the bands are
sensitive to the torsion angle the C_6 rings make with respect to the plane defined
by the nitrogen atoms [25,29].

Excitation of leucoemeraldine solutions in N-methylpyrrolidone (NMP) with
bandgap light produces an intense luminescence peak at 3.5 eV [30], Fig. 6. The
magnitude of the luminescence intensity decreases linearly with increasing
concentration of imine groups within the polymer chain. The luminescence is
nearly zero when the emeraldine base oxidation state is achieved. The decay

time for the luminescence has been measured and found to be ~ 4ns at room
temperature [30]. The presence of a similar luminescence in three-ring
oligomers [30] and also in the aniline ($C_6H_5NH_2$) monomer [31] supports that the
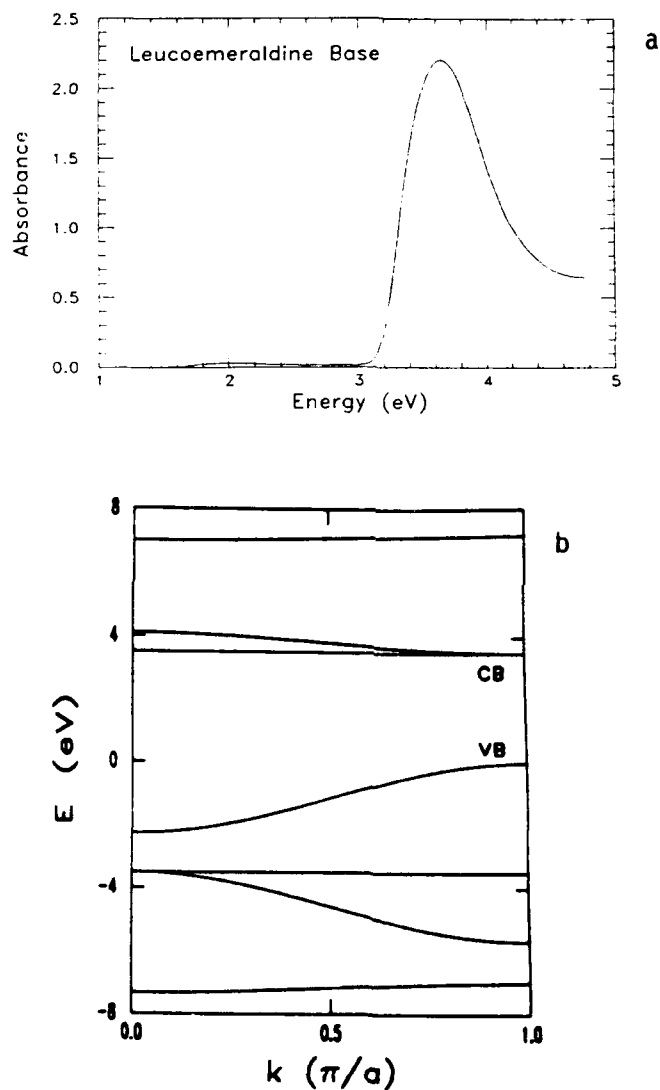luminescence derives from radiative decay of an intramonomer polaronic exciton
[32].

Fig. 5.(a) Absorption
spectrum of leucoemeraldine
base in NMP (from Ref. 33);
(b) Hückel electronic band
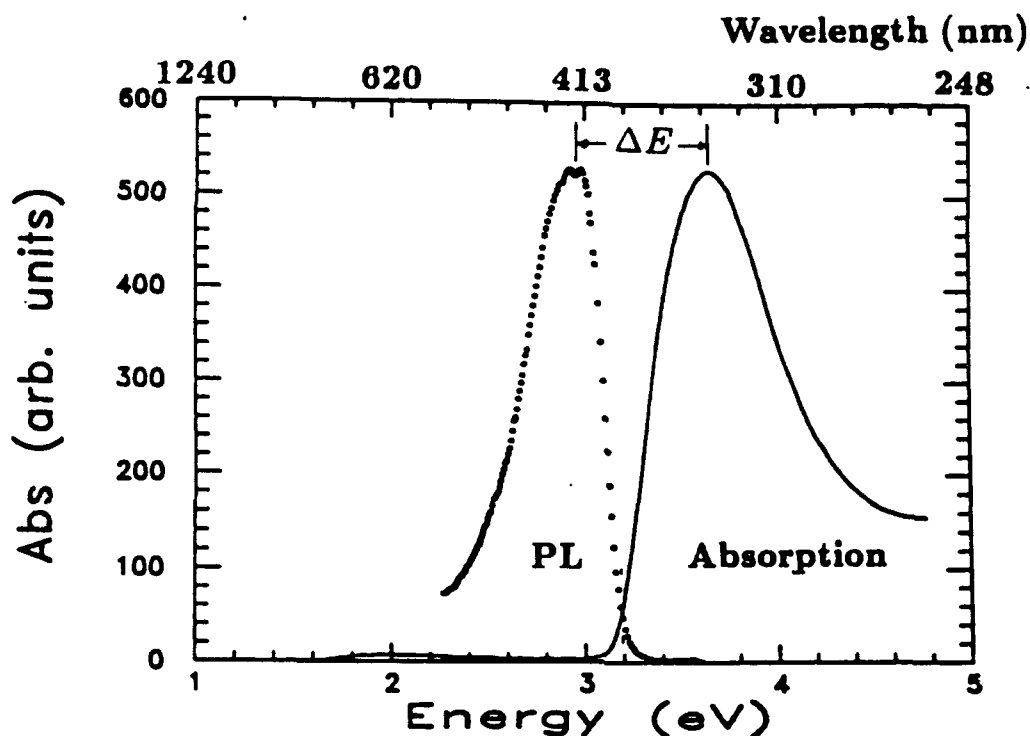structure of leucoemeraldine
(from Ref. 25).

Fig. 6. Absorption and photoluminescence spectra for leucoemeraldine base in NMP, the exciting wavelength for the PL spectrum is ~345 nm (from Ref. 30).

Photoexcitation of LEB films and powders with superbandgap light leads to new intragap absorptions centered at 0.7 eV and 2.9 eV [24,33]. This photoinduced absorption has been described in terms of formation of a ring rotation polaron [24-26, 33]. Because of the large charge conjugation asymmetry in the system there is only one energy level introduced into the gap by the distortion of the ring torsion angles. This polaron differs substantially from earlier studied polarons in polythiophene and polypyrrole and their derivatives in that it has a very large effective mass (~50m_e) due to the effects of a large moment of inertia involved in rotating the polyaniline rings about the N-N axis. Also observed in the photoexcitation spectrum is a bleaching at ~2.0 eV associated with the presence of some residual imine groups in the otherwise pure LEB. At long times a photoinduced absorption at ~1.4 eV is stable. This absorption is associated with a ring rotation polaron trapped adjacent to a quinoid ring. This trapped ring rotation polaron is readily observed in the photoexcitation spectra of emeraldine base [24,33]. Comparison of the magnitude of the photoinduced *ir* active vibrations and electronic absorption confirms the large mass of the photoexcited defects.

The optical absorbance of pernigranilne base though similar to that of EB is different in origin. In particular, the 2.3 eV absorption in PNB has been assigned to the excitation across a Peierls energy gap. This Peierls gap has been proposed to arise from two independent contributions, variation in bond length order parameter and variation in ring torsion angle order parameter, [25,34,35]. The effects of these two order parameters recently have been shown to vary additively [29]. Steady state photoinduced absorption experiments show the presence of a photoinduced charge defect of effective $\sim 5\ m_e$ and a photoinduced charge defect of effective mass $\sim 300m_e$. Because of the enormous difference in their effective mass and their lifetimes, the low energy peak is associated with a solitonic defect in the bond length order parameter while the middle energy peak is associated with a polaronic defect in the ring torsion angle order parameter [36]. Light induced electron spin resonance studies support these assignments [37]. This is the first known material where two order parameters contribute independently to the bandgap and sustain separate excitations.

CHARGE TRANSPORT

The increase in conductivity of emeraldine salt fiber as a function of elongation ratios (l/l_0) demonstrates the importance of orientation and crystallinity (which increases with stretch ratio [13-15]). The conductivity, $\sigma(T) \sim \exp[-(T_0/T)^{\frac{1}{2}}]$ suggests the relevance of two models: quasi-one-dimensional variable range hopping (VRH) [21, 22,38] and hopping of charge carriers between granular metallic regions [39]. The dc conductivity of the hydrochloric salt of poly(orthotoluidine) (POT-ES) has the same temperature dependence but with a six-fold larger T_0 indicative of greater localization of the charge carriers. The thermoelectric power for POT-ES shows only a term for variable range hopping without any temperature range where a metallic-like thermopower dominates [21,22]. Self-doped sulfonated polyaniline (SPAN) [19] provides a similar case study.

The temperature dependence of the microwave frequency (6.5GHz) dielectric constant for unoriented emeraldine hydrochloride (PAN-ES) [40], POT-ES [21,22] and self-doped sulfonated polyaniline [41], Fig. 7, graphically illustrates the importance of interchain interaction in delocalization. Analysis of these data and the data for stretch oriented emeraldine hydrochloric film [30] suggests that the localization length for positive charges in SPAN-ES is $\sim 6A$ while that for POT-ES is $\sim 8A$. Both of these systems have conductivity dominated by quasi-one-dimensional variable range hopping. In contrast, PAN-ES has a parallel localization length in the order of 50A and a perpendicular localization length $\sim 20A$ even at low temperatures [38]. These dimensions which coincide with the estimated size of the crystalline regions strongly support that the three-dimensional delocalization of charge carriers occurs within the crystalline regions of PAN-ES.
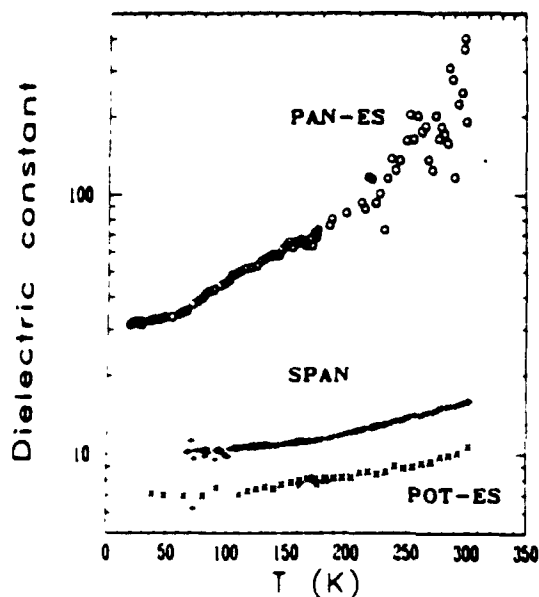
Fig. 7. Microwave frequency dielectric constant vs.
temperature for unoriented PAN-ES (from Ref.38)
unoriented POT-ES (from Ref. 22) and sulfonated
polyaniline (from Ref. 41).

SUMMARY

The varied chemistry and ability of the polyanilines to be processed together
with their environmental stability makes the systems suitable for scientific and
technological studies. Several important concepts have emerged including the
essential roles of ring rotations in electronic phenomena, and three-dimensional
order for high conductivity. These materials remain a laboratory for study of
chemical, physical, and technological opportunities in conducting polymers.

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